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SHORT-TERM TEMPORAL VARIATION IN PM$_{2.5}$ MASS AND CHEMICAL COMPOSITION DURING THE ATLANTA SUPERSITE EXPERIMENT, 1999

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ABSTRACT

Measurements in urban Atlanta of transient aerosol events in which $PM_{2.5}$ mass concentrations rapidly rise and fall over a period of 3-6 hours are reported. The data are based on new measurement techniques demonstrated at the EPA Atlanta Supersite Experiment in August 1999. These independent instruments for aerosol chemical speciation of nitrate, sulfate, ammonium, organic and elemental carbon, reconstructed the observed hourly dry $PM_{2.5}$ mass to within typically 20% or better. Data from the experiment indicate that transient $PM_{2.5}$ events were ubiquitous in Atlanta and were typically characterized by a sudden increase of elemental (soot) and organic carbon in the early morning or sulfate in the late afternoon. The frequent temporal decoupling of these events provides insights into their origins, suggesting mobile sources in metro Atlanta as the main contributor to early morning $PM_{2.5}$ and more regionally located point SO_2 sources for afternoon $PM_{2.5}$ events. The transient events may also have health implications. New data suggest that short-term $PM_{2.5}$ exposures may lead to adverse health effects.[1] Standard integrated filter-based techniques used in $PM_{2.5}$ compliance monitoring networks and in most past $PM_{2.5}$ epidemiological studies collect samples over 24-hour periods and thus are unable to capture these transient events. Moreover, health-effects studies that focus on daily $PM_{2.5}$ mass alone cannot evaluate the health implications of the unique and variable chemical properties of these episodes.

INTRODUCTION

PM$_{2.5}$ includes all particles with aerodynamic diameters less than 2.5 µm. These particles scatter and absorb light, interact with and affect clouds, and deposit within human respiratory systems. Their presence in the atmosphere has been linked to the formation of haze and changes in the atmosphere's radiative balance[2], as well as adverse affects on human health, crops, and materials[3]. In the case of human health effects, epidemiological studies suggest a connection between increases in the mass concentration of PM$_{2.5}$ (typically expressed in units of µg m^{-3}) and increased morbidity and mortality through pulmonary and cardiovascular diseases in susceptible populations.[4-7] The identification of the role of various PM constituents in PM-toxicity is an area of active current research. One major focus has been on combustion emissions, such as soot and organic carbon from mobile sources and sulfates from coal-fired power generators.[8]

For the most part, the association between PM$_{2.5}$ and human health has been established through epidemiological studies in which ambient aerosol concentrations were monitored by collecting particles on filters over extended time periods (e.g, 24 hours) and then using standard analytical techniques to determine the total mass and composition of the collected particles. The U.S. Environmental Protection Agency (EPA) has promulgated two National Ambient Air Quality Standards for PM$_{2.5}$, one based on a maximum 24-hour averaged concentration of 65 µg m^{-3} and the other on an annual average of 15 µg m^{-3}.[9] However, shorter-term, acute exposures caused by a rapid increase in PM$_{2.5}$ concentrations and/or an increase in one chemical component may also have adverse health effects. Historically, characterization of the effects of such transient exposures has been problematic due to measurement limitations. This situation is

changing as a result of the development of near real-time aerosol monitors. For example a recent study using high-resolution measurements of $PM_{2.5}$ mass suggests that short-term spikes in $PM_{2.5}$ mass can trigger the onset of myocardial infarction within a few hours of a pollution event.[1] The effective mitigation of fine particle pollution and its harmful effects on human health and the environment requires an understanding of the sources and properties of these particles as well as the processes that determine these properties. This work attempts to elucidate some of these key aspects of $PM_{2.5}$ in a relatively polluted urban environment by analyzing the near real-time measurements of $PM_{2.5}$ mass concentration and chemical composition gathered during the Atlanta Supersite Experiment.

EXPERIMENTAL METHODS

The Atlanta Supersite Experiment was conducted from August 3, 1999 to September 1, 1999 at a ground-based site located in a mixed residential and industrial neighborhood approximately 4-km northwest of downtown Atlanta. An overview of the experiment is provided by Solomon et al.[10] As part of this experiment, a wide range of instrumentation for both aerosol and gas-phase measurements was deployed. This included a variety of instruments capable of near real-time quantification of $PM_{2.5}$ mass and chemical composition with a time resolution of 1 hour or less. Among the $PM_{2.5}$ chemical components measured by these so-called semi-continuous instruments were sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), and elemental carbon (EC, soot, or black carbon). Some of the instruments used were designed to measure only one $PM_{2.5}$ component (e.g., sulfate), others were designed to measure multiple components (e.g., OC and EC, or numerous aerosol ions). Results from

intercomparisons of the various semi-continuous instruments for the measurement of nitrate and sulfate, and OC and EC are reported elsewhere. [11, 12] The data used for this paper are based on averaging various semi-continuous measurements of the same species. The acronyms used to identify the institutions operating the instruments are defined at end of this paper and are those used in the intercomparison papers where a more complete description of the instrumentation is provided.[11, 12] The ammonium reported here is, for example, the average of the two semi-continuous ammonium techniques deployed during the experiment, both based on ion chromatograph (IC) analysis [13, 14] (operated by ECN and GT/BL, respectively). Sulfate and nitrate are the average of three IC-based detectors (ECN, GT/BL, and TT) and a flash vaporization approach [15] (ADI). Reported OC is the average of an *in situ* thermal-optical carbon analyzer [16] (RU/OGI), the Rupprecht and Patashnick (R&P, Albany NY) 5400 ambient carbon analyzer and a flash vaporization carbon analyzer (ADI). The RU/OGI and R&P 5400 also measured EC, which was also averaged with EC inferred from a Radiance Research particle soot absorption photometer (PSAP, Seattle, WA, operated by ARA) and the Magee Scientific AE-16 aethalometer (Boulder CO, operated by HSPH).

Near real-time dry $PM_{2.5}$ mass was measured during the Atlanta experiment using a TEOM® (R&P, Albany NY) with the sensor heated to 50°C to drive off condensed water.[17] The TEOM® measures the mass collected on a small filter oscillating at the end of a hollow glass tube through which sample air is drawn. Changes in the natural frequency of this oscillation are related to changes in filter mass. Possible aerosol volatility artifacts associated with running the TEOM® at the high temperature of 50°C are discussed in the following section.

Our analysis of data from these instruments indicate that transient $PM_{2.5}$ events are frequent in Atlanta and have specific chemical signatures that provide clues to their sources and may have specific health consequences.

RESULTS AND DISCUSSION

Mass Closure

Before analyzing the data from the near real-time instrumentation for insights into the characteristics of $PM_{2.5}$ during the Atlanta experiment, the completeness and precision of the chemical speciation is assessed by testing for mass closure. This is done by comparing the sum of the measured chemical components to an independent gravimetric measurement of the total dry mass. Since OC measurements only quantify the carbon component of OC, mass closure requires a correction factor to convert mass of carbon to mass of organic compounds; i.e,

$$OM = OC \text{ x (correction factor)} \tag{1}$$

where OC is the measured mass of organic C in $PM_{2.5}$ and OM is the estimated total organic mass of the organic compounds (including O, N, etc) in $PM_{2.5}$. The correction factor is the average organic molecular weight per carbon weight. In keeping with many previous investigators, a correction factor of 1.4 is assumed. Values as high as 1.6±0.2 for urban aerosols are reasonable.[18] Heating the TEOM® sensor (i.e., filter) to obtain a dry $PM_{2.5}$ mass measurement can result in an underestimate of $PM_{2.5}$ mass due to loss of volatile aerosol components and may offset to some extent the use of a low correction factor for OC.

In general, the agreement between the reconstructed mass, using the measurements for the $PM_{2.5}$ constituents and the directly measured $PM_{2.5}$ is quite good. For the entire study period, the mean $PM_{2.5}$ mass and standard deviation obtained from summing the chemical components was 29.5 ± 10.8 µg m^{-3}, while the mean and standard deviation obtained with the TEOM® was 30.9 ± 11.7 µg m^{-3}. The average mass obtained from the TEOM® itself was about 4% lower than that obtained from the integrated filter samplers used during the study.[19]

Higher resolution measurements can more rigorously assess mass closure. For the one-month study, Figure 1 shows the average diurnal $PM_{2.5}$ concentration and its major chemical constituents. Comparison of the sum of the major constituents to the measured $PM_{2.5}$ mass reveals generally good agreement. The largest discrepancies are found at 0900 EST when the reconstructed mass exceeds the measured mass by about 10%, and after 1400 EST when the measured mass exceeds the reconstructed mass by about 7 to 12%. Nonetheless, a similar 24-hour trend is seen in both sets of measurements.

Mass reconstruction based on the 1-hour data for the one-month study is shown in Figure 2. This figure shows that even when the comparison is made using the hourly-averaged data the agreement is generally 20% or better, although exceptions having discrepancies of 40% or more occurred on occasion. Pearson product linear regression of the sum of OM, EC, NO_3^-, SO_4^{2-}, and NH_4^+ versus $PM_{2.5}$ in µg m^{-3} is:

$$\text{Speciated Sum} = 2.78 \pm 0.93 + 0.89 \pm 0.03 \text{ x } PM_{2.5}, \ r^2 = 0.879 \qquad (2)$$

where the uncertainties are based on 95% confidence intervals. Although this is the first

chemical mass reconstruction at 1-hour time resolution over an extended period of time,

the agreement may be somewhat fortuitous due to compensating errors between the

speciated sum and the mass measurement. At the very least, the 1- hour reconstruction

shown in Figure 2 demonstrates consistency between these diverse instruments and their

ability to document the occurrence and chemical characteristics of short-term, transient

$PM_{2.5}$ mass variations.

Transient Characteristics of Atlanta $PM_{2.5}$ Aerosol During the Supersite Experiment

In Atlanta, based on measurements extending over a one-year period, total carbon

(OM + EC), and sulfate each typically comprises about 35 to 45% of the $PM_{2.5}$ dry mass,

with the remainder being composed primarily of ammonium and nitrate[20]. The daily

averages for the one-month Supersite Experiment, shown in Figure 1, are consistent with

these more general yearly trends.

Figure 1 indicates that on average, $PM_{2.5}$ exhibited relatively modest variations

(of 20% or less) over a diurnal cycle during the Atlanta experiment. On the other hand,

the hourly-averaged data from the semi-continuous monitors, illustrated in Figures 3b and

4b, indicate that the variations on short time scales were quite large. In several instances,

$PM_{2.5}$ was observed to vary by factors of 2 to 3 over time intervals of a few hours. Since

SO_4^{2-} and EC+OM are the two major components of $PM_{2.5}$, the short-term variations in

$PM_{2.5}$ illustrated in Figures 3b and 4b are most likely associated with variations in SO_4^{2-}

and EC+OM. Interestingly however, the results illustrated in Figure 1 suggest that, at

least on average, SO_4^{2-} and EC+OM appear to vary independently of each other with

SO_4^{2-} tending to peak in the late afternoon and EC+OM peaking in the morning. In the analyses presented below we examine these tendencies in more detail.

Multivariate Analysis. An objective assessment of the contributions of SO_4^{2-} and EC+OM to variations in $PM_{2.5}$ can be obtained through a multivariate analysis in which a linear regression is used to simultaneously apportion the variances in $PM_{2.5}$, SO_4^{2-} and EC+OM to a number of underlying factors.[21] The relative importance of each factor to each variable is then indicated by the so-called "loading", derived for that variable and factor. A positive (negative) loading indicates that the variable is positively (negatively) correlated to that factor and a small loading indicates that the variable is not affected by that factor. The square of a loading for any given factor and variable is the fraction of the total variance in that variable that can be explained by that factor.

Table 1 summarizes the results of a multivariate analysis involving the 1-hour averaged values observed for $PM_{2.5}$, SO_4^{2-} and EC+OM. This analysis shows that about 97% of the total variance in $PM_{2.5}$ mass can be explained by two independent factors; one being most strongly associated with SO_4^{2-} and the other with EC+OM.

Transient Events. A feature revealed by a higher time-resolution measurement is the presence of short-term transient events. A comparison in Figures 3 and 4 of the variation in $PM_{2.5}$ mass and its chemical components as a function of time using 1-hour and 24-hour averages demonstrates this. It is apparent that, on time scale of hours, $PM_{2.5}$ was highly variable and that the use of 24-hour averages largely masks this variability. For example, on August 10, the 1-hour averaged $PM_{2.5}$ dry mass reached 70.7 µg m^{-3}, the highest value attained during the study and almost double the 24-hour average mass for the day of 37.2 µg m^{-3} (this episode is labeled as 1s in Figure 3b and Table 2). From the

onset of the event to the time of peak concentration (roughly 4 hours), the 1-hour average

$PM_{2.5}$ increased from 29.0 to 70.7 $\mu g\ m^{-3}$. A recent study linking transient $PM_{2.5}$ events

to health effects suggests that a rapid change in $PM_{2.5}$ mass may be as or more important

to health than the peak concentration reached during the episode.[1] Inspection of Figures

3 and 4 reveals that the Atlanta data is replete with similar, albeit less intense, short-term

events that appear in the 1-hour but not in the 24-hour averages.

The timing and chemical nature of the transient $PM_{2.5}$ events provide clues to

their origin. In Atlanta, the aerosol chemical speciation data and our multivariate

analysis shows that in most cases the variability is driven by variations in either OC plus

EC or in sulfate, and as shown by the daily averages (Figure 1), as well as the

multivariate analysis, they tend to vary independently. For example, in Figures 3b and

4b, four episodes in which OM (recall, OM = 1.4 x OC) and EC drive the $PM_{2.5}$ mass

peak are identified as 1c – 4c. Likewise, four events when the $PM_{2.5}$ peak is driven by a

sulfate increase are identified as 1s – 4s. Three events when the peak $PM_{2.5}$ was driven

by simultaneous increases in all three components are labeled as A – C. Pertinent

parameters associated with these events are summarized in Table 2. Combined, Table 2

and Figures 3 and 4 show that the OM plus EC events often begin to develop in the early

morning and peak between 0600 and 0800 EST. Transient OM plus EC events were

rarely observed in the afternoon. In contrast, most sulfate events typically occur in mid

to late afternoon (1500-1700 EST), however, a few events did occur in the early morning

at the time of the OM plus EC events.

It is generally believed that these EC peaks with accompanying OC are from

primary pollutants emitted directly into the atmosphere [22], while sulfate is a secondary

pollutant generated photochemically from the oxidation of SO_2.[23] Daily peaks will also depend on meteorological considerations. For example, after sunset, surface radiative cooling causes increased atmospheric stability and development of a low-level inversion. This tends to limit dispersion of surface-emitted pollutants, and causes their near-surface concentrations to accumulate (e.g., EC and primary OC). After sunrise, however, surface heating promotes turbulence and downward mixing of air from above. This expands the surface layer and dilutes near-surface concentrations of locally emitted pollutants. However, it increases the likelihood of spikes in the near-surface concentration of pollutants from more distant emissions by mixing upper level air down to the surface. Consistent daily patterns in wind speed and direction may also play a role in producing the events. These trends are generally consistent with the following hypothesis: the transient EC and OM (OC) events are from urban mobile sources and sulfate from the more distant tall-stacks of coal-fired power plants that surround the Atlanta metropolitan area.

Implications of Transient Events, Aerosol Acidity and Possible Health Effects

During the carbonaceous events, the fraction of total carbon (EC + OM) to $PM_{2.5}$ varied between 54 to 58%, compared to the study-average of 43%. For the sulfate events, the sulfate mass fractions ($SO_4^=/PM_{2.5}$) varied between 55 to 63%, and the study average was 44%. A consequence of the high sulfate concentrations during these events is typically a 4-fold increase in the $PM_{2.5}$ apparent acidity, shown in Table 2. Here, apparent acidity is the difference in the measured concentrations of anions and cations, all expressed in equivalents. Since the inorganic composition of the $PM_{2.5}$ aerosol during the study was dominated by sulfate and ammonium (see Figure 1), the apparent acidity is

well-represented by 2 x sulfate – ammonium. Alternatively, the molar ratio of ammonium to sulfate can be calculated from the measured concentrations. For the 1-month study the average NH_4^+/SO_4^{2-} molar ratio was 1.7, close to neutral ammonium sulfate, $(NH_4)_2SO_4$. The four episodes identified as 1s, 2s, 3s, and 4s, in Figures 3b and 4b, had ammonium-to-sulfate molar ratios between 1 to 0.7.

The differing diurnal patterns of specific $PM_{2.5}$ chemical components may be important from a health-effects and epidemiological study point-of-view. For example, the late afternoon sulfate events occur when people tend to be active and results in exposure to high $PM_{2.5}$ acidity that accompanies these episodes.[7] Moreover, there may be synergistic interactions with ozone that also typically peaks in the late afternoon in Atlanta and in other urban areas. In terms of epidemiological studies, the differing diurnal trends of $PM_{2.5}$ carbonaceous and sulfate mass could be used in a health effects study similar to Peters et al.[1] to relate transient $PM_{2.5}$ health effects to specific aerosol chemical components. Previous epidemiological studies were ill suited to identify these effects. This is because 24-hour filter sampling times would fail to resolve these transient episodes and their diurnal trends, and the studies were based on reported daily health statistics.

SUMMARY

Newly developed instrumentation for high time resolution measurements of aerosol chemical composition and mass deployed at the EPA Atlanta Supersite show that transient events in which $PM_{2.5}$ mass concentrations rapidly rise and fall over a period of 3-6 hours frequently occur. The contributions of these components to PM-induced toxicity is poorly understood and a scientific issue of much current interest. In Atlanta,

these events are driven primarily by peaks in the carbonaceous and/or sulfate components of $PM_{2.5}$. These components have different sources and generally impact the $PM_{2.5}$ mass concentration at different times of the day. A recent epidemiological study suggests transient $PM_{2.5}$ events can have adverse health effects[1], however current $PM_{2.5}$ monitoring networks using 24-hour averaged filter samples are unable to resolve such events.

The spatial extent of the EC plus OC and sulfate events described here and their ultimate impact on the magnitude and character of the $PM_{2.5}$ exposure of citizens living in metropolitan areas such as Atlanta can not be determined from this study alone. However, future studies involving the deployment of real-time chemical speciation monitors at a number of sites throughout the metropolitan area could better define the scale of these events. Combined with meteorological measurements, this network could help in identifying specific sources responsible for the transient events. The measurements could also be combined with relevant real-time epidemiological data to assess possible health impacts on the metropolitan population.

ACRONYMS

ECN: Netherlands Energy Research Foundation

GT/BL: Georgia Institute of Technology and Brookhaven National Laboratory

TT: Texas Institute of Technology

ADI: Aerosol Dynamics Inc.

RU/OGI: Rutgers Universtiy and Oregon Graduate Institute

ARA: Atmospheric Research and Analysis

HSPH: Harvard School of Public Health

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DISCLAIMER

Figure Captions

Figure 1. Atlanta Supersite experiment average concentrations for August 4 to August 31, 1999 based on hourly averaged data from the semi-continuous detectors. Organic Matter (OM) is the measured organic carbon (OC) multiplied by 1.4.

Figure 2. $PM_{2.5}$ mass reconstruction from Atlanta Supersite measurements. Dry $PM_{2.5}$ (TEOM$^{®}$ sensor heated to 50°C) is compared to the sum of the sulfate, nitrate, ammonium, OC times 1.4, and EC. The top plot shows the percent difference between speciated sum and mass. Data are 1-hour averages.

Figure 3. Chemical composition of the fine aerosol compared to the total $PM_{2.5}$ mass for the first half of the Supersite experiment. Plot a) shows results from a 24h average and b) 1h average. In plot b), specific events in which the peak in $PM_{2.5}$ is driven by sulfate (1s – 4s) and by EC+OM (1c –4c) are shown in the graph. Table 1 summaries pertinent measurements at these times. Note that in some cases, the EC+OM events are also associated with sulfate, examples are labeled with letters A-C

Figure 4. Same as Figure 3, except for the second half of the Supersite experiment.

Table 1. Factor Loadings Derived From Multivariate Analysis Of 1-Hour Averaged $PM_{2.5}$, SO_4^{2-}, and EC+OM

A. Assuming 2 Factors			
Variable	Factor 1[a]	Factor 2[a]	
$PM_{2.5}$	0.90	0.38	
SO_4^{2-}	0.99	--	
EC+OM	0.43	0.90	
B. Assuming 3 Factors			
Variable	Factor 1[a]	Factor 2[a]	Factor 3[a]
$PM_{2.5}$	0.89	0.37	0.25
SO_4^{2-}	0.98	--	--
EC+OM	0.41	0.91	--

[a]Factor loadings that explain less than 5% of the variance in any variable were deemed to not be significant and have been replaced by "--."

Table 2. Pertinent Parameters Recorded During Transient Episodes Identified In Figures 3 and 4.

Label	Day of Aug. 1999	Hour at Peak EST	$PM_{2.5}$ µg m^{-3}	$SO_4^=$ µg m^{-3}	NO_3^- µg m^{-3}	NH_4^+ µg m^{-3}	OC µgC m^{-3}	EC µgC m^{-3}	Acidity[a] neq m^{-3}	$SO_4^=$/PM	TC/PM[b]
1c	7	6:30	43.1	11.8	0.9	NA	11.8	7.8	NA	0.27	0.56
2c	12	8:30	53.9	14.3	1.3	4.0	15.0	10.9	99	0.27	0.59
3c	18	7:30	37.8	11.4	0.6	3.0	10.7	5.5	79	0.30	0.54
4c	27	7:30	48.6	14.2	1.9	4.8	12.2	9.4	65	0.29	0.54
1s[c]	10	17:00	60.2	37.7	0.2	6.8	8.1	2.1	439	0.63	0.22
2s	16	15.:30	46.8	25.6	0.6	5.1	8.3	2.5	262	0.55	0.30
3s	17	15:30	50.8	30.8	0.3	4.0	7.6	2.0	421	0.61	0.25
4s	20	15:30	60.1	35.8	0.4	5.2	9.9	3.1	465	0.60	0.28
A	6	6:30	65.7	27.6	0.9	NA	12.2	8.7	NA	0.42	0.39
B	21	7:30	45.0	21.9	3.1	7.9	8.1	3.9	67	0.49	0.34
C	30	22:30	33.8	13.6	0.2	4.0	7.1	1.7	63	0.40	0.34

[a] The apparent acidity equals $2SO_4^= + NO_3^-$ - NH4$^+$ with all concentrations expressed in nmole m^{-3}.
[b] TC/PM is the total carbon (OC x 1.4 + EC) divided by fine aerosol mass ($PM_{2.5}$)
[c] Since the sulfate peaked 1 h prior to the $PM_{2.5}$ in this case, the average over 2 hours is given here. At 16:30 the sulfate peak was 41.2 µg m^{-3} and the $PM_{2.5}$ 49.8 µg m^{-3}, in the following hour, 17:30, the sulfate was 34.2 µg m^{-3} and $PM_{2.5}$ 70.7 µg m^{-3}.
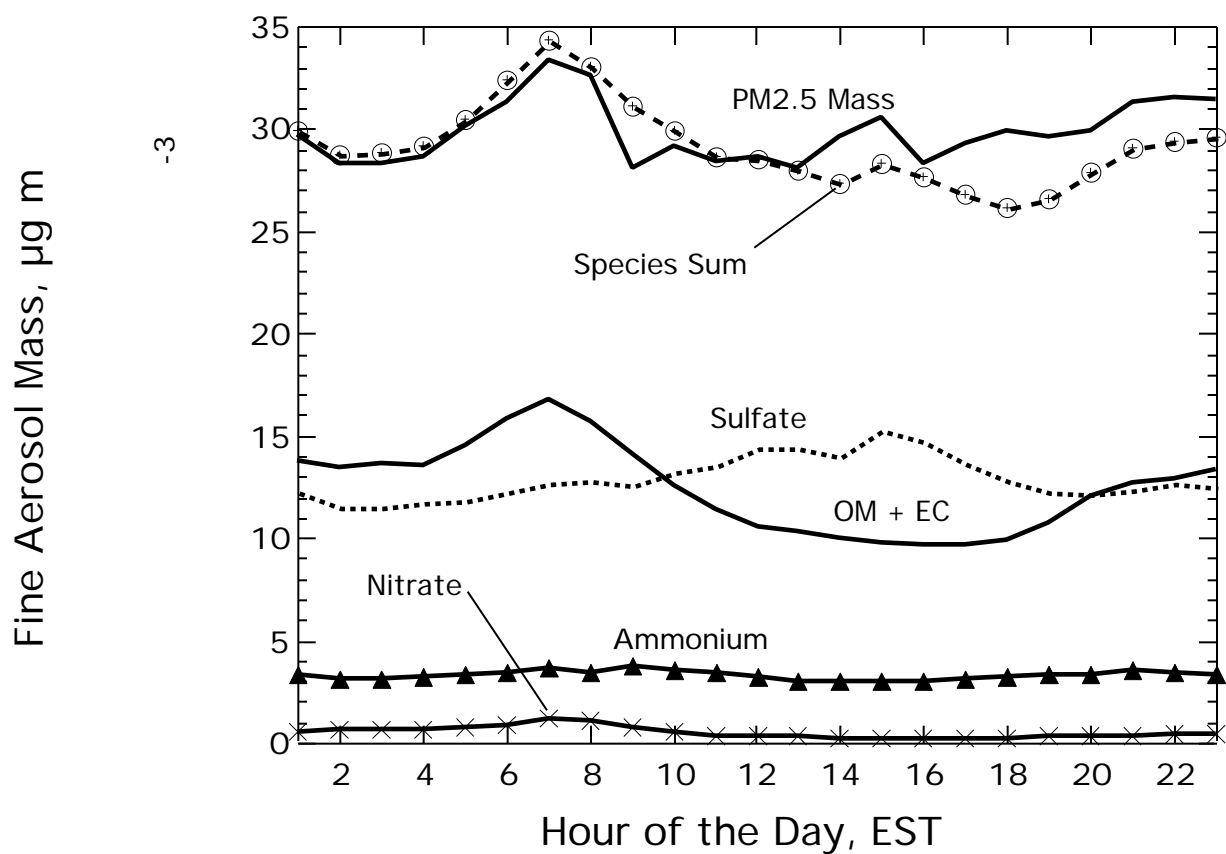
Figure 1. Atlanta Supersite experiment average concentrations for August 4 to August 31, 1999 based on hourly data from the semi-continuous detectors. Organic Matter (OM) is the measured organic carbon (OC) multiplied by 1.4.
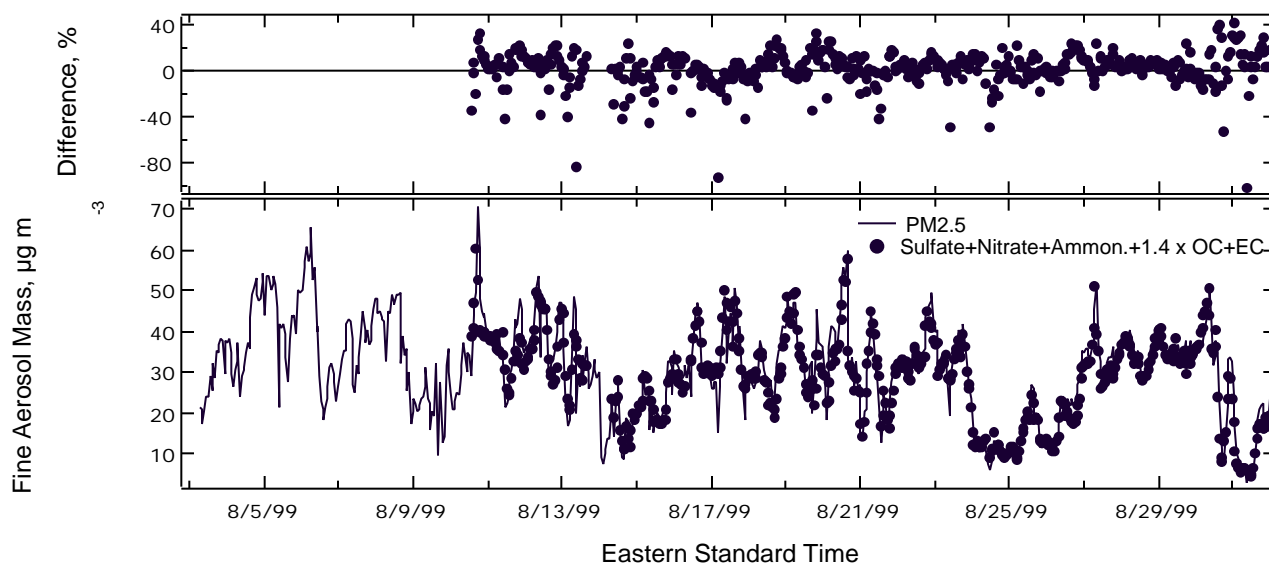
Figure 2. PM$_{2.5}$ mass reconstruction from Atlanta Supersite measurements. Dry PM$_{2.5}$ (TEOM® sensor heated to 50°C) is compared to the sum of the sulfate, nitrate, ammonium, OC times 1.4, and EC. The top plot shows the percent difference between speciated sum and mass. Data are 1-hour averages.
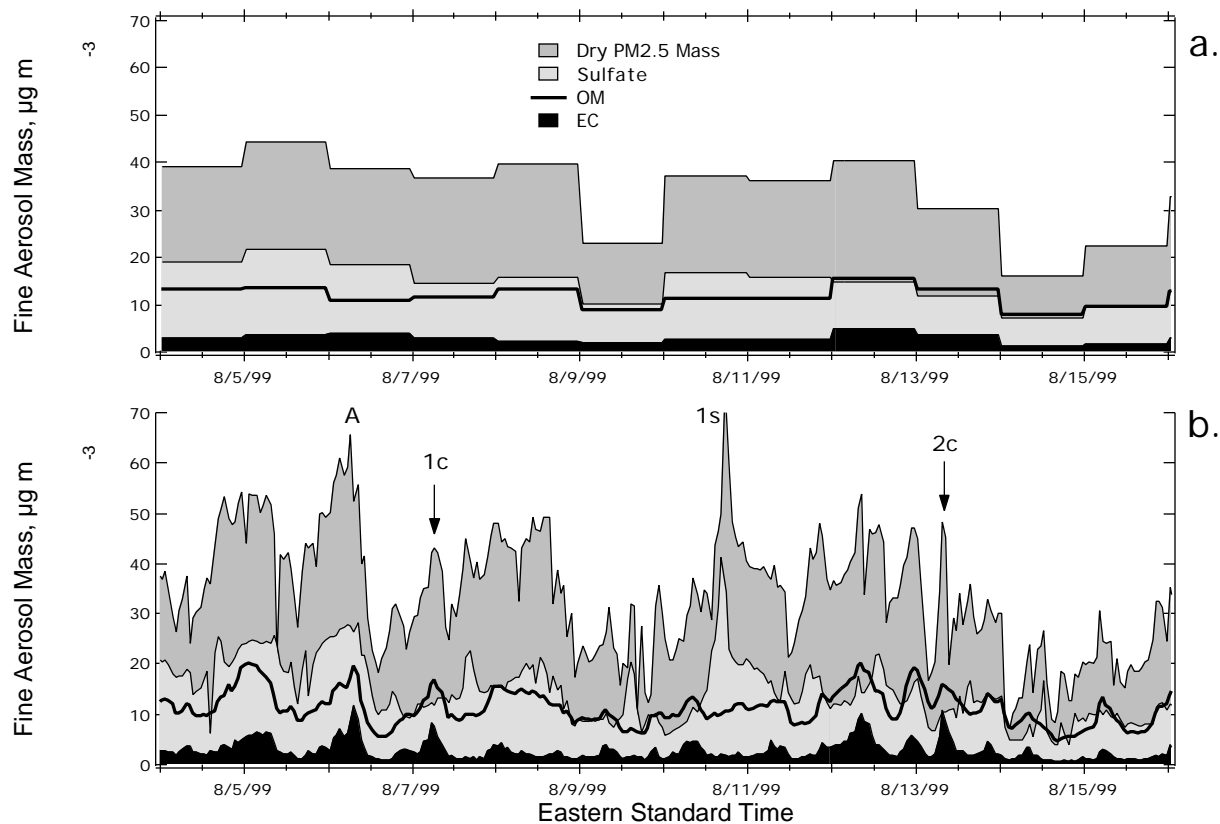
Figure 3. Chemical composition of the fine aerosol compared to the total PM$_{2.5}$ mass for the first half of the Supersite experiment. Plot a) shows results from a 24h average and b) 1h average. In plot b), specific events in which the peak in PM$_{2.5}$ is driven by sulfate (1s – 4s) and by EC+OM (1c –4c) are shown in the graph. Table 1 summaries pertinent measurements at these times. Note that in some cases, the EC+OM events are also associated with sulfate, examples are labeled with letters A-C.
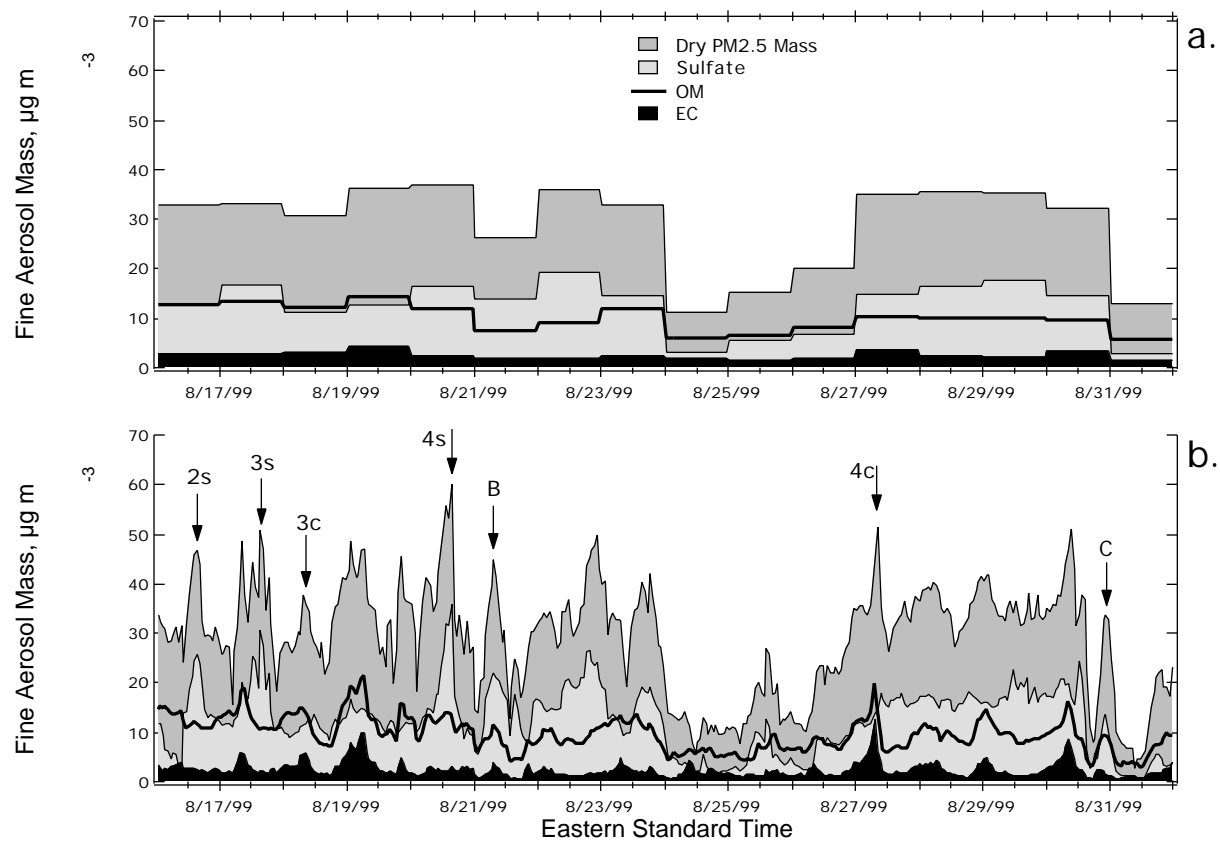
Figure 4. Same as Figure 3, except for the second half of the Supersite experiment.